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WHAT IS CLAIMED IS:

1. A process for cross-linking sulfonyl groups of a sulfonated polymers wherein at least a fraction of the cross-linking bonds bear an ionic charge, the process comprising contacting the polymer with the cross-linking agent allowing the reaction between two 5 sulfonyl groups from adjacent polymeric chains, to form the said cross-linking bonds.
2. Process according to claim 1 wherein the cross-linking bonds are of the type:
 $P-SO_2-Y(M^+)-SO_2-P'$; or
 $P-SO_2(M^+)Y-SO_2-(Q-SO_2)_rY(M^+)SO_2-P'$
- 10 wherein
 - P and P' are the same or different and are part of a polymeric chain;
 - Y comprises N or CR wherein R comprises H, CN, F, SO_2R' , C_{1-20} alkyl substituted or unsubstituted; C_{1-20} aryl substituted or unsubstituted; C_{1-20} alkylene substituted or unsubstituted, wherein the substituent comprises one or more halogen, and wherein the 15 chain comprises one or more substituent F, SO_2R , aza, oxa, thia or dioxathia;
 - R' comprises F, C_{1-20} alkyl substituted or unsubstituted; C_{1-20} aryl substituted or unsubstituted; C_{1-20} alkylene substituted or unsubstituted, wherein the substituent comprises one or more halogens;
 - M^+ comprises an inorganic or organic cation;
- 20 - Q comprises a divalent radical C_{1-20} alkyl, C_{1-20} oxaalkyl, C_{1-20} azaalkyl, C_{1-20} thiaalkyl, C_{1-20} aryl or C_{1-20} alkylaryl, each being optionally substituted by one or more halogens, and wherein the chain comprises one or more substituents oxa, aza or thia; and
 - r is 0 or 1.

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3. Process according to claim 2 wherein M⁺ comprises the proton, a metal cation, an organometallic cation or an organic cation optionally substituted with one or more organic radicals comprising:

- a proton, an alkyl, an alkenyl, an oxaalkyl, an oxaalkenyl, an azaalkyl, an azaalkenyl,
- 5 a thiaalkyl, a thiaalkenyl, a dialkylazo, a silaalkyl optionally hydrolysable, a silaalkenyl optionally hydrolysable, each being straight, branched or cyclic and comprising from 1 to 18 carbon atoms;
- a cyclic or heterocyclic aliphatic radical comprising from 4 to 26 carbon atoms optionally comprising at least one lateral chain comprising one or more heteroatoms such
- 10 as nitrogen, oxygen or sulfur;
- an aryl, an arylalkyl, an alkylaryl and an alkenylaryl of from 5 to 26 carbon atoms optionally comprising one or more heteroatoms in the aromatic nucleus or in a substituent.

- 15 4. Process according to claim 3 wherein the metal comprises an alkaline metal, an alkaline-earth metal, a rare earth or a transition metal; the organic metallic cation comprises metallocenium, an arene-metallocenium, an alkylsilyl, an alkylgermyl or an alkyltin, and the organic cation comprises R["]O⁺ (onium), NR^{"+} (ammonium), R["]C(NHR["])₂⁺ (amidinium), C(NHR["])₃⁺ (guanidinium), C₅R["]N⁺ (pyridinium), C₃R["]N₂⁺ (imidazolium), C₂R["]N₃⁺ (triazolium), C₃R["]N₂⁺ (imidazolium), SR^{"+} (sulfonium), PR^{"+} (phosphonium), IR^{"+} (iodonium), (C₆R["])₂C⁺ (carbonium), wherein R["] is defined as an organic radical as defined above, and when an organic cation comprises at least two radicals R["] different from H, these radicals can form together a cycle, aromatic or not, eventually containing the center bearing the cationic charge.

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5. Process according to claim 2 wherein the divalent radical and the sulfonated polymer are partially or completely fluorinated.

6. Process according to claim 1, wherein a leaving group is linked to the sulfonyl groups before performing the cross-linking.

7. Process according to claim 6 wherein the leaving group comprises F, Cl, Br, an electrophilic heterocycle N-imidazolyl, N-triazolyl, R²SO₃, R² being an organic radical optionally halogenated, the organic radical comprising:

10 - a proton, an alkyl, an alkenyl, an oxaalkyl, an oxaalkenyl, an azaalkyl, an azaalkenyl, a thiaalkyl, a thiaalkenyl, a dialkylazo, a silaalkyl optionally hydrolysable, a silaalkenyl optionally hydrolysable, each being straight, branched or cyclic and comprising from 1 to 18 carbon atoms;

15 - a cyclic or heterocyclic aliphatic radical comprising from 4 to 26 carbon atoms optionally comprising at least one lateral chain comprising one or more heteroatoms such as nitrogen, oxygen or sulfur;

- an aryl, an arylalkyl, an alkylaryl and an alkenylaryl of from 5 to 26 carbon atoms optionally comprising one or more heteroatoms in the aromatic nucleus or in a substituent.

20

8. Process according to claim 2 wherein the cross-linking agent comprises an organometallic comprising organo-lithium, organo-magnésium, magnesium or organo-aluminium, or a compound of general formula:

(M⁺)A₂Y⁻;

25 (M⁺)AY⁻SO₃Y⁻A(M⁺);

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wherein Y, Q and M are as defined above, and A comprises M, Si(R'), Ge(R'), or Sn(R'),
wherein R' is C₁₋₁₈ alkyle.

5 9. Process according to claim 8 wherein A comprises a trialkylsilyl group.

10 10. Process according to claim 8 wherein the cross-linking agent comprises Li₃N;
C₃Al₄; [(CH₃)₂Si]₂NLi (or Na or K); NH₃ + 3 DABCO;
CF₃SO₂C[(CH₃)₂Si][Li(TMEDA)]₂; (CH₃)₂CNH₂ + 3 TEA; NH₂SO₂NH₂ + 4 TEA;
10 [[(CH₃)₂Si](Li)N]₂SO₂; [(TMEDA)(Mg)N]₂SO₂; CH₃Li; (CH₃)₂Al; NH₂Li (or Na or K);
[[Si(CH₃)₃](Li)NSO₂]₂CF₃; [Li[Si(CH₃)₃]NSO₂CF₃]₂CF₃; [(Li)Si(CH₃)₃NSO₂CF₃];
[Li[Si(CH₃)₃]NSO₂CF₃CF₂]₂O; SO₂Cl₂ + 3 DABCO; SO₂(imidazole); [FSO₂CF₂]₂ + 3
TEA; (ClSO₂CF₂)CF₂ + 3 DABCO and (FSO₂CF₂CF₃)₂O + 3 DABCO.

15 11. Process according to claim 1 wherein the non cross-linked polymer is molded
before being cross-linked.

12. Process according to claim 1 wherein the non cross-linked polymer is
mechanically blended with the cross-linking agent, pressed and heated.

20

13. Process according to claim 1 wherein the non cross-linked polymer is molded
and contacted with a solution of the cross-linking agent in an inert solvent.

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14. Process according to claim 13 wherein the cross-linking density is controlled by the time of immersion in the solvent, the temperature of the solvent, or the cross-linking agent concentration in the solvent.

5 15. Process according to claim 13 wherein the solvent comprises aromatic hydrocarbons, hydrocarbons and aliphatic ethers partially or completely halogenated, THF, alkylethers of mono-, di-, tri- and tetraethylene glycols (glymes), tertiary alkylamides including DMF, N-methylpyrrolidone, tetramethylurea and its cycling analogues, N-alkylimidazoles, tetraalkylsulfamides, and mixture thereof.

10

16. Process according to claim 2 wherein the non cross-linked polymer is molded and contacted with the cross-linking agent and a non cross-linking ionogene agent to form end groups $-\text{SO}_3^-(\text{M}^+)$, or $-[\text{SO}_2\text{YSO}_2\text{R}]^-(\text{M}^+)$, R being an organic radical as defined above, preferably halogenated, and particularly perfluorinated.

15

17. Process according to claim 16 wherein the non cross-linked polymer is molded and contacted sequentially or simultaneously with the cross-linking agent and the non cross-linking ionogene agent.

20

18. Process according to claim 16 wherein the non cross-linking ionogene agent comprises $(\text{CH}_3)_3\text{SiO}^-(\text{M}^+)$ or $[(\text{CH}_3)_3\text{SiNSO}_2\text{CR}_f]^-(\text{M}^+)$ wherein M^+ is as defined above and R_f is an alkyl, oxaalkyl, azaalkyl or thiaalkyl radical essentially perfluorinated and comprising from 1 to 12 carbon atoms.

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19. Process according to claim 1 wherein a reinforcing agent is added to the polymer before the cross-linking.

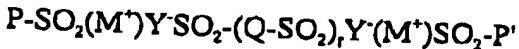
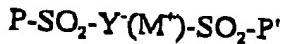
20. An electrochemical cell wherein a membrane comprising a cross-linked 5 polymer according to claim 1 is used as a solid electrolyte.

21. A cell according to claim 20 comprising a fuel cell, a water electrolyser, an alkali-chloride cell, an acid or salts electrochemical cell, or an ozone-producing cell.

10 22. A cell according to claim 21 forming an element of a fuel cell wherein M^+ is a hydrated proton and the positive electrode comprises an oxygen reducing catalyst.

15 23. A sulfonated polymer comprising in whole or in part cross-linked sulfonyl groups, and wherein at least a fraction of the cross-linking bonds bear an ionic charge.

24. A polymer according to claim 23 wherein the cross-linking bonds are of the type:



20 wherein

- P, P', Y, Q, M⁺ and r are as defined in claim 2.

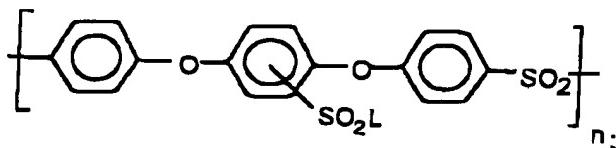
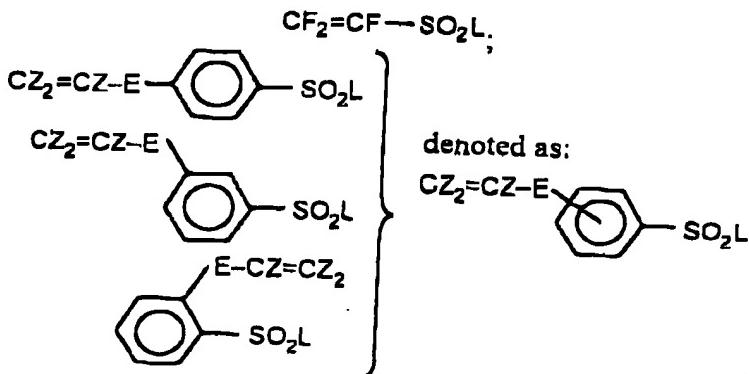
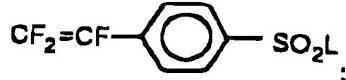
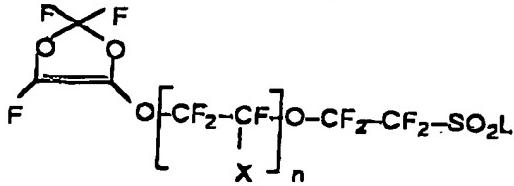
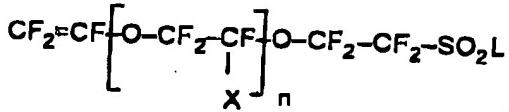
25 25. A polymer according to claim 24 wherein M⁺ comprises the proton, a metal cation, an organometallic cation or an organic cation optionally substituted by one or more organic radical comprising:

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- a proton, an alkyl, an alkenyl, an oxaalkyl, an oxaalkenyl, an azaalkyl, an azaalkenyl, a thiaalkyl, a thiaalkenyl, a dialkylazo, a silaalkyl optionally hydrolysable, a silaalkenyl optionally hydrolysable, each being straight, branched or cyclic and comprising from 1 to 18 carbon atoms;
 - 5 - a cyclic or heterocyclic aliphatic radical comprising from 4 to 26 carbon atoms optionally comprising at least one lateral chain comprising one or more heteroatoms such as nitrogen, oxygen or sulfur;
 - an aryl, an arylalkyl, an alkylaryl and an alkenylaryl of from 5 to 26 carbon atoms optionally comprising one or more heteroatoms in the aromatic nucleus or in a
10 substituent.
26. A polymer according to claim 25 wherein the metal comprises an alkaline metal, an alkaline-earth metal, a rare earth or a transition metal; the organic metallic cation comprises metallocenium, an arene-metallocenium, an alkylsilyl, an alkylgermyl
15 or an alkyltin, and the organic cation comprises $R''O^+$ (onium), NR'''^+ (ammonium), $R''C(NHR'')_2^+$ (amidinium), $C(NHR'')_3^+$ (guanidinium), $C_5R''N^+$ (pyridinium), $C_3R''N_2^+$ (imidazolium), $C_2R''N_3^+$ (triazolium), $C_3R''N_2^+$ (imidazolinium), SR'''^+ (sulfonium), PR'''^+ (phosphonium), IR'''^+ (iodonium), $(C_6R'')_2C^+$ (carbonium), wherein R'' is defined as an
organic radical as defined above, and when an organic cation comprises at least two
20 radicals R'' different from H, these radicals can form together a cycle, aromatic or not, eventually containing the center bearing the cationic charge.
27. A polymer according to claim 24 wherein the divalent radical and the sulfonated polymer are partially or completely fluorinated.

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28. A polymer according to claim 23 derived from at least of the following monomers:



wherein

- 15 - X is F, Cl or CF₃;
- n varies between 0 and 10 inclusively;
 - E is absent, O, S, SO₂;
 - Z is H or F; and
 - L is a leaving group.

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29. A polymer according to claim 23 further comprising a reinforcing agent.

30. The use of a cross-linked polymer according to claim 23 in an alkali-chloride
5 electrolysis process, as a separator in an electrochemical preparation of organic and
inorganic compounds, as a separator between an aqueous and organic phase, or as a
catalyst for Diels-Alder additions, Friedel-Craft reactions, aldol condensation, cationic
polymerisation, esterifications and acetal formations.